Journal of Magnetic Resonance 214 (2012) 68–75

Contents lists available at SciVerse ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Use of composite refocusing pulses to form spin echoes

Smita Odedra, Stephen Wimperis *

School of Chemistry and WestCHEM, University of Glasgow, Glasgow G12 8QQ, United Kingdom

ARTICLE INFO

Article history:
Received 24 August 2011
Revised 6 October 2011
Available online 19 October 2011

Keywords:
Composite pulses
Symmetry
B_1 inhomogeneity
Resonance offset
Phase cycling
Pulse imperfections

ABSTRACT

The radiofrequency pulses used in NMR are subject to a number of imperfections such as those caused by inhomogeneity of the radiofrequency (B_1) field and an offset of the transmitter frequency from precise resonance. The effect of these pulse imperfections upon a refocusing pulse in a spin-echo experiment can be severe. Many of the worst effects, those that distort the phase of the spin echo, can be removed completely by selecting the echo coherence pathway using either the "Exorcycle" phase cycle or magnetic field gradients. It is then tempting to go further and try to improve the amplitude of the spin-echo signal by replacing the simple refocusing pulse with a broadband composite 180° pulse that compensates for the relevant pulse imperfection. We show here that all composite pulses with a symmetric or asymmetric phase shift scheme will reintroduce phase distortions into the spin echo, despite the selection of the echo coherence pathway. In contrast, all antisymmetric composite pulses yield no phase distortion whatsoever, both on and off resonance, and are therefore the correct symmetry of composite refocusing pulse to use. These conclusions are verified using simulations and ^{31}P MAS NMR spin-echo experiments performed on a microporous aluminophosphate.

1. Introduction

Many NMR experiments yield a lower signal intensity than expected on account of pulse imperfections, such as inhomogeneity of the radiofrequency (B_1) field or an offset of the transmitter frequency from the resonance frequency. In addition, the NMR spectrum may be adversely affected in other ways by these pulse imperfections, with the appearance of signals with distorted phase or poorly suppressed unwanted signals. In general, the more pulses there are in an experiment, the worse these problems become.

The advent of broadband composite pulses, i.e., composite pulses that were designed to self-compensate for one or more of the common pulse imperfections, promised to solve many of these problems [1–18]. However, although they have been spectacularly successful in one or two specialist applications, such as heteronuclear decoupling in liquids [19–21], composite pulses have largely failed to achieve the expected improvements when used in multiple-pulse NMR experiments. Anecdotally, what one often hears is: "I tried using a composite pulse and there was no improvement – in fact, it was slightly worse."

The purpose of this paper is to examine the use of broadband composite 180° pulses in forming spin echoes. Pulse imperfections affect refocusing pulses very strongly and so this is probably the most important practical example to consider. It is reasonably well known that the phase properties of the early broadband composite pulse $90°_{90°}180°_{0°}90°_{90°}$ [1,2] make it ill-suited for use as a refocusing pulse in a spin-echo experiment. Here, we additionally demonstrate that the majority of so-called phase-distortionless or constant-rotation composite pulses [5,10,12,15,16] are also not ideal for this application. We show that, as with refocusing elements used to tailor the excitation profile for, e.g., solvent-peak suppression [22], one must pay careful attention to the symmetry of the broadband composite 180° pulse used.

2. Theory

2.1. Spin echoes, pulse imperfections, and coherence pathway selection

Consider a magnetization vector of unit length that has undergone free precession with an offset Ω for a time τ and so acquired a phase $\phi = \Omega\tau$. We can write this vector $I_x \cos\phi + I_y \sin\phi$. To form a spin echo we must reverse the phase ϕ by applying a 180° pulse to the rotating frame x axis:

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{180°_x} I_x \cos\phi - I_y \sin\phi \quad (1)$$

Note that we are using the shorthand "arrow notation" of Ref. [23] to describe rotations. The phase of the magnetization is now

$$\arctan\left(\frac{-\sin\phi}{\cos\phi}\right) = \arctan(-\tan\phi) = -\phi \quad (2)$$

as desired. A further period of free precession of duration τ will yield a vector with zero phase and a perfect spin echo will be formed.

* Corresponding author. Fax: +44 141 3304888.
E-mail address: stephen.wimperis@glasgow.ac.uk (S. Wimperis).

1090-7807/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jmr.2011.10.006

A common pulse imperfection is flip angle misset, arising either from poor pulse calibration or, more fundamentally, from a spatial inhomogeneity of the B_1 field. We can model this by considering a refocusing pulse with a general flip angle β:

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\beta_x} I_x \cos\phi + I_y \sin\phi\cos\beta + I_z \sin\phi\sin\beta \quad (= \mathrm{A}) \tag{3}$$

The phase of the magnetization vector is now

$$\arctan\left(\frac{\sin\phi\cos\beta}{\cos\phi}\right) = \arctan(\tan\phi\cos\beta) \tag{4}$$

and this is only equal to $-\phi$ if $\beta = 180°$ and so, in general, a perfect spin echo will not form. Furthermore, as the magnetization phase depends on the flip angle β there may be significant signal cancellation in an inhomogeneous B_1 field. The amplitude of the signal is given by $(\cos^2\phi + \sin^2\phi\cos^2\beta)^{1/2}$ and so, in general, is less than unity and depends on ϕ and β. The presence of magnetization along the z axis in Eq. (3) is also undesirable if further pulses are to be applied.

Partial solutions to these problems are well known and are based on the concept of coherence pathway selection [24]. We need to select only the components of the magnetization vector after the imperfect pulse that will form a perfect spin echo and to discard the components that will not echo. This can be achieved using either phase cycling or magnetic field gradients and it is the former method that will be described here in detail. The phase cycle for partly correcting the imperfections of a refocusing pulse is known as "Exorcycle" and, in its original implementation, consists of repeating the spin-echo experiment four times, each time advancing the phase of the refocusing pulse by 90° [25]. So, in addition to Eq. (3), we have:

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\beta_y} I_x \cos\phi\cos\beta - I_z \cos\phi\sin\beta + I_y \sin\phi \quad (= \mathrm{B}) \tag{5a}$$

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\beta_{\bar{x}}} I_x \cos\phi + I_y \sin\phi\cos\beta - I_z \sin\phi\sin\beta \quad (= \mathrm{C}) \tag{5b}$$

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\beta_{\bar{y}}} I_x \cos\phi\cos\beta + I_z \cos\phi\sin\beta + I_y \sin\phi \quad (= \mathrm{D}) \tag{5c}$$

The magnetization from the four experiments is added and subtracted alternately and the result of this can be written:

$$\mathrm{A} - \mathrm{B} + \mathrm{C} - \mathrm{D} = 2I_x \cos\phi(1 - \cos\beta) - 2I_y \sin\phi(1 - \cos\beta) \tag{6}$$

The phase of the magnetization is now

$$\arctan\left(\frac{-\sin\phi(1 - \cos\beta)}{\cos\phi(1 - \cos\beta)}\right) = \arctan(-\tan\phi) = -\phi \tag{7}$$

and so a perfect spin echo will be formed. The averaged amplitude of the magnetization vector is $(1 - \cos\beta)/2$, which is less than unity if $\beta \neq 180°$ but no longer depends on the phase ϕ. The magnetization along the z axis has been cancelled. These properties of Exorcycle, that the magnetization phase is corrected perfectly but that the amplitude retains a strong dependence on the flip angle of the refocusing pulse, are exploited in the "depth pulse" application for spatial localization [26]. (Note that a "three-step Exorcycle" also exists [24], using 120° phase shifts, but that it is less general than the original version as only one of the two possible echo coherence pathways is selected.)

Another common pulse imperfection is the presence of a resonance offset, which inevitably arises when there is more than one chemically shifted resonance in the NMR spectrum and only a single transmitter frequency. A resonance offset has two effects on the refocusing pulse: the rotation axis is tilted up towards the z axis and the effective flip angle increases. We have already considered the latter, so we can model the former problem by considering a $180°_x$ refocusing pulse with a rotation axis tilted up towards the z axis by an angle Δ (which is equivalent to a Δ rotation about the rotating-frame y axis, then a 180° rotation about the x axis, and finally a Δ rotation about the $-y$ axis):

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta_y} \xrightarrow{180°_x} \xrightarrow{\Delta_{\bar{y}}} I_x \cos\phi\cos 2\Delta + I_z \cos\phi\sin 2\Delta - I_y \sin\phi \quad (= \mathrm{E}) \tag{8}$$

In this case the phase of the magnetization vector is

$$\arctan\left(\frac{-\sin\phi}{\cos\phi\cos 2\Delta}\right) = \arctan\left(\frac{-\tan\phi}{\cos 2\Delta}\right) \tag{9}$$

and this is only equal to $-\phi$ if $\Delta = 0$ (i.e., if the pulse is on resonance) and so, in general, a perfect spin echo will not form. The amplitude of the signal is given by $(\cos^2\phi\cos^2 2\Delta + \sin^2\phi)^{1/2}$ and so, in general, is less than unity and depends on ϕ and Δ.

As with pulse flip angle misset, we can try Exorcycle to partly fix these problems. So, in addition to Eq. (8), we have:

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta_{\bar{x}}} \xrightarrow{180°_y} \xrightarrow{\Delta_x} -I_x \cos\phi + I_y \sin\phi\cos 2\Delta + I_z \sin\phi\sin 2\Delta \quad (= \mathrm{F}) \tag{10a}$$

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta_{\bar{y}}} \xrightarrow{180°_{\bar{x}}} \xrightarrow{\Delta_y} I_x \cos\phi\cos 2\Delta - I_z \cos\phi\sin 2\Delta - I_y \sin\phi \quad (= \mathrm{G}) \tag{10b}$$

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta_x} \xrightarrow{180°_{\bar{y}}} \xrightarrow{\Delta_{\bar{x}}} -I_x \cos\phi + I_y \sin\phi\cos 2\Delta - I_z \sin\phi\sin 2\Delta \quad (= \mathrm{H}) \tag{10c}$$

and we find

$$\mathrm{E} - \mathrm{F} + \mathrm{G} - \mathrm{H} = 2I_x \cos\phi(1 + \cos 2\Delta) - 2I_y \sin\phi(1 + \cos 2\Delta) \tag{11}$$

The phase of the magnetization is now

$$\arctan\left(\frac{-\sin\phi(1 + \cos 2\Delta)}{\cos\phi(1 + \cos 2\Delta)}\right) = \arctan(-\tan\phi) = -\phi \tag{12}$$

and so a perfect spin echo will be formed. The amplitude of the magnetization vector is $(1 + \cos 2\Delta)/2$, which is less than unity if $\Delta \neq 0$. The magnetization that appears along the z axis in Eq. (8) has been cancelled.

Finally, we can consider one last imperfection of the refocusing pulse: the rotation axis deviates from the correct one but remains in the xy plane. This is not an imperfection that occurs with simple pulses but, as we will see, is relevant to many composite pulses. We can model this problem by considering a $180°_x$ refocusing pulse with a rotation axis tilted towards the y axis by an angle Δ' (which is equivalent to a Δ' rotation about the $-z$ axis, then a 180° rotation about the x axis, and finally a Δ' rotation about the z axis). In this case, the four steps of Exorcycle yield:

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta'_{\bar{z}}} \xrightarrow{180°_x} \xrightarrow{\Delta'_z} I_x \cos(\phi - 2\Delta') - I_y \sin(\phi - 2\Delta') \quad (= \mathrm{I}) \tag{13a}$$

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta'_{\bar{z}}} \xrightarrow{180°_y} \xrightarrow{\Delta'_z} -I_x \cos(\phi - 2\Delta') + I_y \sin(\phi - 2\Delta') \quad (= \mathrm{J}) \tag{13b}$$

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta'_{\bar{z}}} \xrightarrow{180°_{\bar{x}}} \xrightarrow{\Delta'_z} I_x \cos(\phi - 2\Delta') - I_y \sin(\phi - 2\Delta') \quad (= \mathrm{K}) \tag{13c}$$

$$I_x \cos\phi + I_y \sin\phi \xrightarrow{\Delta'_{\bar{z}}} \xrightarrow{180°_{\bar{y}}} \xrightarrow{\Delta'_z} -I_x \cos(\phi - 2\Delta') + I_y \sin(\phi - 2\Delta') \quad (= \mathrm{L}) \tag{13d}$$

and we find

$$\mathrm{I} - \mathrm{J} + \mathrm{K} - \mathrm{L} = 4I_x \cos(\phi - 2\Delta') - 4I_y \sin(\phi - 2\Delta') \tag{14}$$

In both Eq. (13a) and Eq. (14) the phase of the magnetization is

$$\arctan\left(\frac{-\sin(\phi - 2\Delta')}{\cos(\phi - 2\Delta')}\right) = -(\phi - 2\Delta') \tag{15}$$

and so the application of Exorcycle has yielded no change to the result in this case: if the deviation from ideality lies in the *xy* plane then rotating the problem about the *z* axis and averaging is ineffective. Of course, the amplitude of the transverse magnetization is still unity in both Eq. (13a) and Eq. (14) (i.e., no *z* magnetization has appeared) but the additional phase of $2\Delta'$ will prevent the formation of a perfect spin echo if it is a function of the B_1 field strength or the resonance offset.

Magnetic field gradients, either pulsed or static, yield a very similar result to that described above for the Exorcycle phase cycle. The only difference is that a B_0 field gradient does not dephase any *z* magnetization produced by the imperfect refocusing pulse and, unless precautions are taken, this unwanted magnetization may reappear as observable signal if further pulses and gradients are applied. One solution is to use the first and third steps of Exorcycle (i.e., phase inversion of the refocusing pulse and summation of the signal) in addition to the field gradients.

2.2. Properties of symmetric and antisymmetric composite pulses

A composite pulse is here defined as a continuous sequence of pulses of constant frequency and B_1 amplitude but differing flip angle and phase. Thus an *N*-element composite pulse can be written:

$$(\beta_1)_{\varphi_1}(\beta_2)_{\varphi_2}\cdots(\beta_N)_{\varphi_N} \tag{16}$$

We are interested here in composite pulses with a symmetric phase shift scheme, those that have $\beta_1 = \beta_N$, $\beta_2 = \beta_{N-1}$, etc. and $\varphi_1 = \varphi_N$, $\varphi_2 = \varphi_{N-1}$, etc., and antisymmetric composite pulses, those that have $\beta_1 = \beta_N$, $\beta_2 = \beta_{N-1}$, etc. and $\varphi_1 = \varphi_0 + \varphi_{1'}$, $\varphi_2 = \varphi_0 + \varphi_{2'}$ $\cdots$ $\varphi_{N-1} = \varphi_0 - \varphi_{2'}$, $\varphi_N = \varphi_0 - \varphi_{1'}$ where the central pulse (if any) has the base phase φ_0. The product of two rotations is another rotation, so any composite pulse always has an overall rotation angle and rotation axis in addition to the flip angles and rotation axes of the individual elements. The symmetry properties of the composite pulse place certain restrictions on the overall rotation axis, as we will now show.

First, we will prove that an on-resonance symmetric composite pulse has an overall rotation axis in the *xy* plane [11,27]. Consider the propagator *U* for a *symmetric* sequence of three *off-resonance* rotations: (i) β about an axis with a phase φ in the *xy* plane and tilted up towards the *z* axis by Δ, (ii) β' about an axis with a phase φ' in the *xy* plane and tilted up towards the *z* axis by Δ, and (iii) β about an axis with a phase φ in the *xy* plane and tilted up towards the *z* axis by Δ:

$$\begin{aligned} U = {} & \exp\{-i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{-i\beta'(I_x\cos\varphi'\cos\Delta + I_y\sin\varphi'\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{-i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \end{aligned} \tag{17}$$

So the inverse propagator is (reverse the order and make all rotations negative)

$$\begin{aligned} U^{-1} = {} & \exp\{i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{i\beta'(I_x\cos\varphi'\cos\Delta + I_y\sin\varphi'\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \end{aligned} \tag{18}$$

If the overall rotation axis of *U* (and U^{-1}) lies in the *xy* plane then a 180° (or π) rotation of U^{-1} about *z* should give *U*:

$$\begin{aligned} & \exp\{-i\pi I_z\}U^{-1}\exp\{i\pi I_z\} \\ & = \exp\{-i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta - I_z\sin\Delta)\} \\ & \quad \times \exp\{-i\beta'(I_x\cos\varphi'\cos\Delta + I_y\sin\varphi'\cos\Delta - I_z\sin\Delta)\} \\ & \quad \times \exp\{-i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta - I_z\sin\Delta)\} \end{aligned} \tag{19}$$

but this is equal to *U* only if $\Delta = 0$ (i.e., the pulses are applied on resonance). There are no special constraints on the rotation axis for an off-resonance symmetric composite pulse. It is clear that this result can be immediately extended to symmetric composite pulses containing an arbitrary number of component pulses.

And, second, we will prove that an antisymmetric composite pulse with a base phase $\varphi_0 = 0$ (i.e., *x* phase) has an overall rotation axis in the *xz* plane, regardless of whether it is applied on or off resonance [11]. Consider the propagator *U* for a *antisymmetric* sequence of three *off-resonance* rotations: (i) β about an axis with a phase φ in the *xy* plane and tilted up towards the *z* axis by Δ, (ii) β' about an axis in the *xz* plane tilted up from the *x* axis towards the *z* axis by Δ, and (iii) β about an axis with phase $-\varphi$ in the *xy* plane and tilted up towards the *z* axis by Δ:

$$\begin{aligned} U = {} & \exp\{-i\beta(I_x\cos\varphi\cos\Delta - I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{-i\beta'(I_x\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{-i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \end{aligned} \tag{20}$$

So the inverse propagator is (reverse the order and make all rotations negative):

$$\begin{aligned} U^{-1} = {} & \exp\{i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{i\beta'(I_x\cos\Delta + I_z\sin\Delta)\} \\ & \times \exp\{i\beta(I_x\cos\varphi\cos\Delta - I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \end{aligned} \tag{21}$$

If the rotation axis of *U* (and U^{-1}) lies in the *xz* plane then a 180° (or π) rotation of U^{-1} about *y* should give *U*:

$$\begin{aligned} & \exp\{-i\pi I_y\}U^{-1}\exp\{i\pi I_y\} \\ & = \exp\{-i\beta(I_x\cos\varphi\cos\Delta - I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} \\ & \quad \times \exp\{-i\beta'(I_x\cos\Delta + I_z\sin\Delta)\} \\ & \quad \times \exp\{-i\beta(I_x\cos\varphi\cos\Delta + I_y\sin\varphi\cos\Delta + I_z\sin\Delta)\} = U \end{aligned} \tag{22}$$

Thus all antisymmetric composite pulses with a base phase $\varphi_0 = 0$ have an overall rotation axis in the *xz* plane for all resonance offsets. More generally, for an antisymmetric composite pulse with a base phase of φ_0, the rotation axis lies in a plane containing the φ_0 axis and the *z* axis.

Since we have shown that Exorcycle or magnetic field gradients can correct for problems with the spin-echo phase that arise from imperfections in the overall flip angle or from the rotation axis deviating from the *x* axis into the *xz* plane (but not if it deviates into the *xy* plane), it is clear that a broadband antisymmetric composite pulse [11,12,15] is the appropriate choice for correcting refocusing pulse imperfections in a spin-echo experiment. This is the central thesis of this paper and we believe it is a significant one, especially in view of the fact that the majority of broadband composite 180° pulses in the literature are either symmetric or asymmetric.

2.3. Multiple refocusing and "excitation sculpting"

It should be mentioned here that it is possible to use an on-resonance symmetric broadband composite 180° pulse to form a spin echo with perfect phase as long as one is prepared to form two consecutive spin echoes with the same composite pulse. In this case, any error in the spin-echo phase caused by the first composite pulse will be automatically corrected by the second. Levitt and Freeman have discussed this in the context of a multiple-echo train formed with the $90°_{90°}180°_{0°}90°_{90°}$ composite pulse, where there is correction of the magnetization phase on even-numbered echoes [28]. However, this self-correction breaks down off resonance where the composite pulse is no longer a rotation in the *xy* plane.

More generally, Hwang and Shaka have shown that the second spin echo formed by any refocusing element – symmetric, antisymmetric or asymmetric – has perfect phase as long as the coherence pathway is selected independently for each of the two identical refocusing elements. This result applies both on and off resonance. They have named this observation "excitation sculpting" [22].

However, neither of these important results is relevant in the present context; if one wishes to correct for pulse imperfections in a simple spin-echo experiment then one should not double the possible sources of imperfection by using two refocusing pulses.

3. Broadband composite 180° pulses

Many broadband composite 180° pulses have been proposed and only a small selection will be introduced here, which are the ones that we will use in our comparative simulations and experiments. These are shown in Table 1, which also gives each of the sequences a temporary shorthand label for convenience of discussion in this work; where there is no label in the original literature we have supplied one that tries to honor the discoverer(s) of the pulse. For a fuller account of the sequences available, the reader is directed to the original literature and to the various reviews [13,17,18].

3.1. Symmetric sequences

The first broadband composite 180° pulse proposed was $90°_{90°}180°_{0°}90°_{90°}$ (designated here LF) [1,2]. This was intended to compensate for B_1 inhomogeneity (or flip-angle misset). It was designed to invert *z* magnetization and no constraint was placed on the overall rotation axis. It is therefore predicted not to work well as a single refocusing element.

A more sophisticated broadband composite 180° pulse is $180°_{120°}180°_{240°}180°_{120°}$ (designated here TS) [5,8]. This is also designed to compensate for B_1 inhomogeneity but also to have an overall rotation axis along the rotating-frame *x* axis across its usable bandwidth. This type of composite pulse is often referred to as being phase distortionless. At the edges of its bandwidth, however, the overall rotation axis of this symmetric sequence will deviate into the *xy* plane.

For compensation of off-resonance effects, the broadband composite 180° pulse $90°_{135°}270°_{45°}90°_{135°}$ (designated here LT) has been proposed [1,2,5]. This has been shown to have an overall rotation axis along the rotating-frame *x* axis across a certain bandwidth and so can be described as phase distortionless.

3.2. Asymmetric sequences

For compensation of B_1 inhomogeneity, the phase-distortionless composite 180° pulse $180°_{104.5°}360°_{313.4°}180°_{104.5°}180°_{0°}$ has been introduced (designated $BB_1(180°)$ in Ref. [16] and simply BB_1 here). This sequence has received much attention in the context of NMR quantum computing where it has been praised for its wide bandwidth, stable rotation axis, and relatively good performance at nonzero resonance offsets [18]. Across its effective bandwidth, the overall rotation axis is along the *x* axis but, as an asymmetric sequence, we have no idea *a priori* what happens to the rotation axis outside this bandwidth, either on or off resonance.

The asymmetric composite 180° pulse $90°_{0°}270°_{180°}360°_{0°}$ (designated W here) has been proposed for the correction of nonzero resonance offsets. It is not of the phase distortionless type [20].

3.3. Antisymmetric sequences

The composite 180° pulses $180°_{46.6°}180°_{255.5°}180°_{0°}180°_{104.5°}180°_{313.4°}$ (designated F_1 in Ref. [15] and here) and $180°_{256°}180°_{52°}180°_{0°}180°_{128°}180°_{0°}180°_{232°}180°_{0°}180°_{308°}180°_{104°}$ (designated TPG here) [11] have been suggested for compensation of B_1 inhomogeneity, with only the former investigated in any detail (the latter was mentioned in an Appendix in Ref. [11], with no results shown; it also exhibits some compensation for off-resonance effects). By their very nature, these antisymmetric sequences are of the phase-distortionless type since the overall rotation axis must lie on or close to the *x* axis within their effective bandwidths as a direct consequence of it being constrained to lie in the *xz* plane. We note in passing that the sequence F_1 can be considered as an "antisymmetrized" version of the asymmetric composite pulse BB_1.

The properties of antisymmetric sequences make new composite 180° pulses with rotation axes in the *xz* plane particularly easy to design. All one has to do is search through the pulse phases of an antisymmetric sequence of 180° pulses for a composite pulse that inverts *z* magnetization over a range of values of (say) the B_1 field. For example, using this approach, implemented in a simple FORTRAN-77 program, we found the 13-pulse composite 180° pulse given in Table 1 (and designated OW here) for compensation of B_1 inhomogeneity. (Note that OW is presented here purely to show that new antisymmetric sequences await discovery, perhaps including ones that are shorter than OW, are compensated for both B_1 inhomogeneity and resonance offset, and that consist of other than 180° pulses.)

For compensation of off-resonance effects, the broadband composite 180° pulse $60°_{180°}300°_{0°}60°_{180°}$ (designated SP here) has been demonstrated, together with longer sequences of the same type with greater bandwidths [12]. This is clearly a symmetric sequence but it is also an antisymmetric sequence as it has $\varphi_1 = \varphi_0 + 180°$, $\varphi_2 = \varphi_0$ and $\varphi_3 = \varphi_0 - 180°$ with $\varphi_0 = 0°$. Therefore,

Table 1
Broadband composite 180° pulses discussed in this work.

Sequence	Type	Compensation	Designation	Ref.
$90°_{90°}180°_{0°}90°_{90°}$	Sym.	B_1 inhomo.	LF	[1,2]
$180°_{120°}180°_{240°}180°_{120°}$	Sym.	B_1 inhomo.	TS	[5,8]
$180°_{104.5°}360°_{313.4°}180°_{104.5°}180°_{0°}$	Asym.	B_1 inhomo.	BB_1	[16]
$180°_{46.6°}180°_{255.5°}180°_{0°}180°_{104.5°}180°_{313.4°}$	Anti.	B_1 inhomo.	F_1	[15]
$180°_{256°}180°_{52°}180°_{0°}180°_{128°}180°_{0°}180°_{232°}180°_{0°}180°_{308°}180°_{104°}$	Anti.	B_1 inhomo.(+ Reson. offset)	TPG	[11]
$180°_{53°}180°_{30°}180°_{304°}180°_{142°}180°_{255°}180°_{309°}180°_{0°}180°_{51°}180°_{105°}180°_{218°}180°_{56°}180°_{330°}180°_{307°}$	Anti.	B_1 inhomo.	OW	This work
$90°_{135°}270°_{45°}90°_{135°}$	Sym.	Reson. offset	LT	[1,2,5]
$90°_{0°}270°_{180°}360°_{0°}$	Asym.	Reson. offset	W	[20]
$60°_{180°}300°_{0°}60°_{180°}$	Anti + Sym.	Reson. offset	SP	[12]

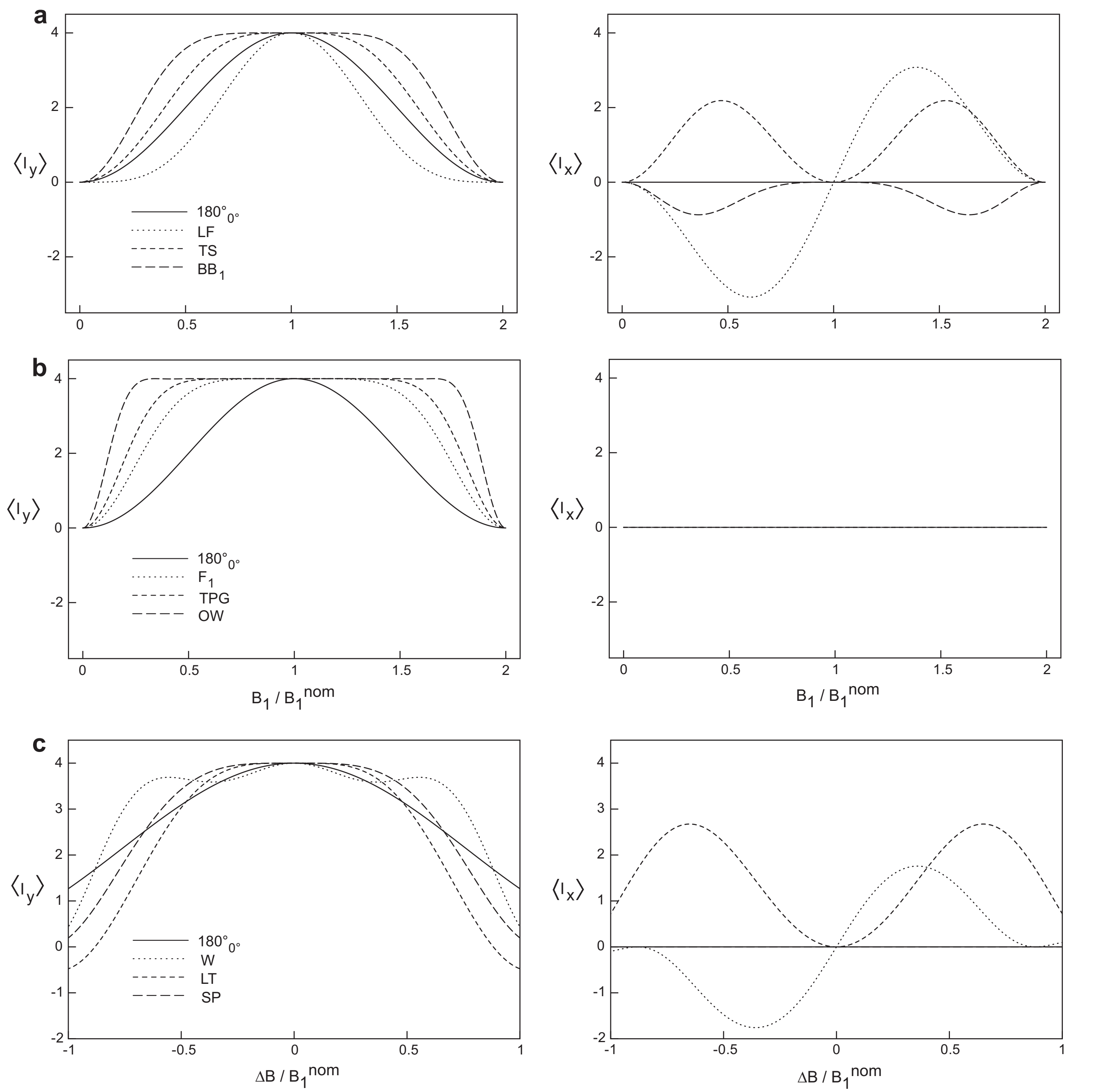

Fig. 1. Simulations of the performance of broadband composite 180° pulses in a spin-echo experiment. The simulations assume an initial state $\sigma^{\text{initial}} = -I_y$ and a refocusing pulse that has been subjected to the four steps of the Exorcycle phase cycle. The in-phase magnetization component $\langle I_y \rangle$ and the unwanted out-of-phase component $\langle I_x \rangle$ are shown as a function of B/B_1^{nom} (to study performance in the presence of B_1 inhomogeneity) or $\Delta B/B_1^{\text{nom}}$ (to study performance in the presence of a resonance offset). (a) Performance of the simple $180°_{0°}$ pulse and the composite pulses LF, TS and BB_1 (see Table 1). Only the simple refocusing pulse (which is technically antisymmetric) yields a zero out-of-phase component. (b) Performance of the simple $180°_{0°}$ pulse and the composite pulses F_1, TPG and OW (see Table 1). All of these antisymmetric sequences yield a zero out-of-phase component. (c) Performance of the simple $180°_{0°}$ pulse and the composite pulses W, LT and SP (see Table 1). Only the two antisymmetric sequences, $180°_{0°}$ and SP, yield a zero out-of-phase component.

we discuss it in the antisymmetric category since it has the favorable properties of this class away from exact resonance.

4. Results

4.1. Simulations

The performance of broadband composite 180° pulses in a spin-echo experiment was simulated assuming an initial state $\sigma^{\text{initial}} = -I_y$ (the result of a perfect $90°_{0°}$ pulse on an I_z state). The phase of the refocusing pulse was incremented through the four steps of Exorcycle and the resulting magnetizations summed appropriately over the four steps such that the ideal result should be $\sigma^{\text{final}} = +4I_y$. We then plotted the desired in-phase magnetization component $\langle I_y \rangle = \text{Tr}\{\sigma^{\text{final}} I_y\}/\text{Tr}\{I_y^2\}$ and the unwanted out-of-phase component $\langle I_x \rangle = \text{Tr}\{\sigma^{\mathit{final}} I_x\}/\text{Tr}\{I_x^2\}$ as a function of B_1/B_1^{nom} (to study performance in the presence of B_1 inhomogeneity) or $\Delta B/B_1^{\text{nom}}$ (to study performance in the presence of a resonance

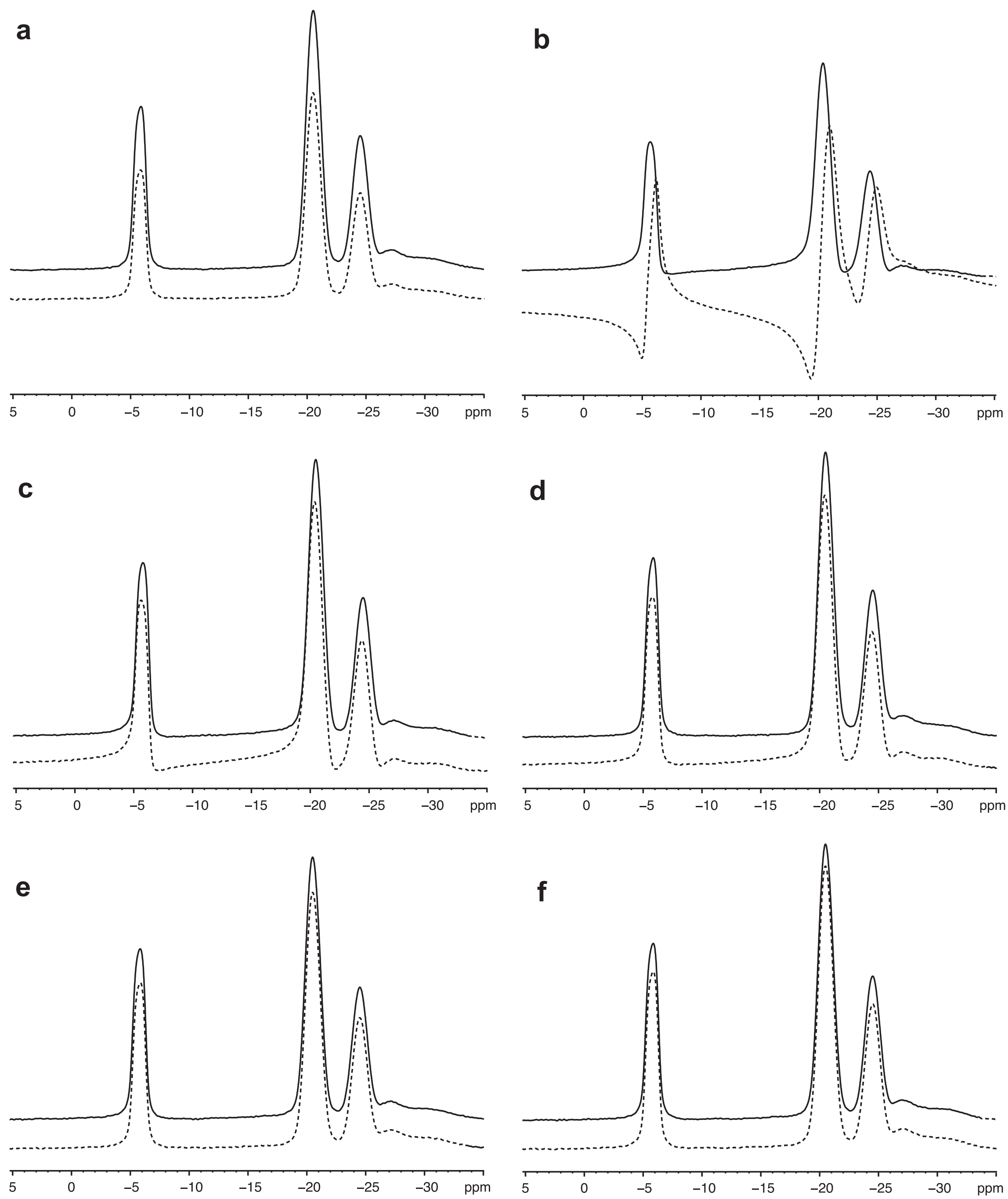

Fig. 2. ^{31}P (162 MHz) MAS NMR spin-echo spectra of AlPO-14 with an isopropylamine template (10 kHz MAS rate, 200 µs total echo interval, 90° pulse duration of 2.40 µs, spin–lattice relaxation interval of 180 s, four-step Exorcycle phase cycle applied to the refocusing pulse). (a) Spectra with well calibrated simple 180° refocusing pulse (solid line) and refocusing pulse set to 67% of the correct duration (dashed line). (b–f) As (a) but using the composite refocusing pulses (b) LF, (c) TS, (d) BB_1, (e) F_1 and (f) TPG (see Table 1). Only the spectra in (a, e and f), which were recorded with antisymmetric refocusing pulses, are free of any phase distortion.

offset), where $\Delta B = -\Omega/\gamma$ is the residual static field in the rotating frame, with the offset of the resonance from the transmitter frequency Ω and the gyromagnetic ratio γ.

Fig. 1a shows the $\langle I_y \rangle$ and $\langle I_x \rangle$ performance of the simple refocusing pulse $180°_{0°}$, the symmetric composite pulses LF and TS, and the asymmetric composite pulse BB_1 as a function of normalized B_1 field strength. Only the simple 180° pulse does not yield an unwanted out-of-phase $\langle I_x \rangle$ component. The composite pulse LF yields a large $\langle I_x \rangle$ component and an $\langle I_y \rangle$ component that is actually narrowband (not broadband) compared with that of a simple pulse; in the presence of B_1 inhomogeneity this sequence will hence perform poorly as a refocusing pulse. The other two so-called phase-distortionless composite pulses have broadband $\langle I_y \rangle$ profiles and $\langle I_x \rangle$ components that are nearly zero very close to B_1^{nom}, the nominal B_1 field strength. However, at B_1 values further away from B_1^{nom} they still yield significant unwanted $\langle I_x \rangle$ components.

In contrast, Fig. 1b shows the $\langle I_y \rangle$ and $\langle I_x \rangle$ performance of the simple refocusing pulse $180°_{0°}$ and the antisymmetric composite pulses F_1, TGP and OW as a function of normalized B_1 field strength. The three composite pulses all have broadband $\langle I_y \rangle$ profiles and, on the account of their antisymmetric design, yield no unwanted $\langle I_x \rangle$ component whatsoever.

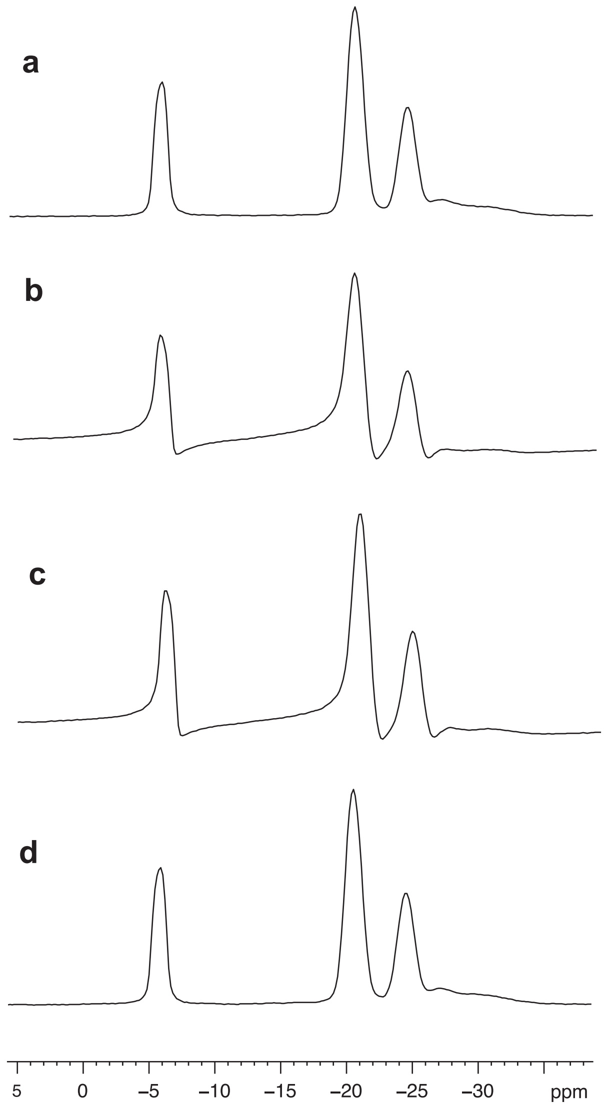

Fig. 3. 25 kHz off-resonance ^{31}P (162 MHz) MAS NMR spin-echo spectra of AlPO-14 with an isopropylamine template (10 kHz MAS rate, 200 μs total echo interval, 90° pulse duration of 2.40 μs, spin–lattice relaxation interval of 180 s, four-step Exorcycle phase cycle applied to the refocusing pulse). (a) Spectrum with well calibrated simple 180° refocusing pulse. (b–d) As (a) but using the composite refocusing pulses (b) LT, (c) W and (d) SP (see Table 1). Only the spectra in (a and d), which were recorded with antisymmetric refocusing pulses, are free of any phase distortion.

Fig. 1c shows the $\langle I_y \rangle$ and $\langle I_x \rangle$ performance of the simple refocusing pulse $180°_{0°}$, the symmetric composite pulse LT, the asymmetric composite pulse W and the antisymmetric composite pulse SP as a function of normalized resonance offset, $\Delta B/B_1^{nom}$. As predicted, only the simple refocusing pulse and the antisymmetric composite pulse SP yield no $\langle I_x \rangle$ component and so only these would generate a spin echo with perfect phase at all offsets.

4.2. Experiments

Experiments were performed on a Bruker Avance 400 NMR spectrometer equipped with a widebore 9.4 T magnet. The ^{31}P MAS NMR spectrum of as-synthesized AlPO-14, which contains isopropylamine as a template molecule, was chosen as the subject of our spin-echo experiments. This choice was made based on the current setup in our laboratory; other nuclei in both the solid and solution state and different probe designs are expected to yield equivalent results. The powdered solid sample was packed in a 4-mm MAS rotor and the spinning rate was 10 kHz. The Larmor frequency was 162 MHz. The calibrated 90° pulse length for ^{31}P was 2.40 μs, corresponding to a nutation rate, $\nu_1 = |\gamma B_1|/2\pi$, of 104 kHz. No ^{1}H decoupling was used.

The pulse sequence used was a 90° – τ – R – τ – spin echo, where R is the simple or composite refocusing pulse. The τ interval was equal to 100 μs (one rotor period) and timed from the center of the 90° pulse to the center of the R refocusing pulse and from the center of the R pulse to the start of data acquisition. In all experiments, the four-step Exorcycle phase cycle was applied to the refocusing pulse R.

For investigations of refocusing pulse performance in the presence of B_1 inhomogeneity, the spin-echo experiment was performed with the transmitter frequency close to the center of the ^{31}P MAS spectrum. With R as a well calibrated simple 180° pulse, the ^{31}P spin-echo spectrum was acquired and phased. The same phase correction was then applied to all subsequent B_1 inhomogeneity experiments. The refocusing pulse R was then replaced with various composite 180° pulses designed to be broadband with respect to B_1, all with correctly calibrated pulse durations. As there will be a significant B_1 inhomogeneity across the sample volume, even for the solenoid coil in a MAS probe, then we might expect to see some changes in signal amplitude and/or phase even with correctly calibrated pulse durations. However, to exacerbate these effects intentionally, the experiments were then repeated with all components of the refocusing pulses misset to two-thirds of their correctly calibrated duration (e.g., a 90° pulse is replaced with a 60° pulse, a 180° pulse replaced with a 120° pulse, etc.). The initial 90° excitation pulse was left unchanged.

Fig. 2a shows the ^{31}P MAS NMR spectra recorded with a simple refocusing pulse. As expected, the spectrum consists of three peaks at −6, −20 and −25 ppm, although there is also a broad impurity peak in this sample around −30 ppm. The spectrum with the correctly calibrated 180° refocusing pulse (solid line) has been phased, as described above. With the same phase corrections, the phase of the spectrum with the misset pulse duration (dashed line) is also correct, as expected with the use of Exorcycle, although the peak amplitudes are reduced. Fig. 2b–f shows the equivalent results for the composite pulses LF (Fig. 2b), TS (Fig. 2c), BB_1 (Fig. 2d), F_1 (Fig. 2e) and TPG (Fig. 2f). With a misset pulse duration, the peak amplitudes are fully restored in Fig. 2c–f. However, peaks with distorted phase are evident in the ^{31}P spectra in Fig. 2b–d, although in the last of these (Fig. 2d) it is only when the BB_1 refocusing pulse is misset (dashed line) that distortions are seen. No phase distortions are observed in any of the spectra in Fig. 2e and f, where the antisymmetric composite pulses F_1 and TPG have been used, even when the pulse durations are misset.

For investigations of refocusing pulse performance in the presence of a resonance offset, spin-echo experiments were performed with the transmitter frequency offset by 25 kHz from the center of the ^{31}P MAS spectrum, yielding an offset parameter $\Delta B/B_1^{nom} \approx 0.25$ for all three peaks in the spectrum. With R as a simple 180° pulse, the ^{31}P spin-echo spectrum was acquired and phased. The same phase correction was then applied to all subsequent experiments. The refocusing pulse R was then replaced with various composite 180° pulses designed to be broadband with respect to offset, all with correctly calibrated pulse durations.

Fig. 3a shows the off-resonance ^{31}P MAS NMR spectrum recorded with a simple refocusing pulse. The spectrum has been phased, as described above. Fig. 3b–d shows the equivalent results for the composite pulses LT (Fig. 3b), W (Fig. 3c) and SP (Fig. 3d). Peaks with distorted phase are evident in the ^{31}P spectra in Fig. 3b and c. No phase distortions are observed in the spectrum in Fig. 3d, where the antisymmetric composite pulse SP has been used.

5. Discussion and conclusions

Pulse imperfections remain a major problem in modern NMR spectroscopy and imaging. Even with a solenoid radiofrequency coil, as used in MAS probes, the B_1 field falls to half its maximum amplitude at the edges of the coil. With saddle coils, as used in solution NMR probes, the problem of B_1 inhomogeneity will be even worse. In solid-state NMR, radiofrequency field strengths of $\sim$100 kHz can be achieved for nuclei such as ^{13}C, ^{19}F or ^{31}P, but the spectra may similarly cover $\sim$100 kHz or more on high-field spectrometers, meaning that offset parameters, $\Delta B/B_1^{nom}$, of 0.5 or greater will be routinely encountered. Again, in solution NMR, the offset problem will be worse on account of the lower radiofrequency field strengths.

Selection of the echo coherence pathway, using Exorcycle or magnetic field gradients, should always be performed when using a 180° refocusing pulse as this will correct for many of its imperfections. However, this pathway selection cannot correct for the loss of signal amplitude that occurs as a result of the resonance offset or B_1 inhomogeneity. The temptation, therefore, is to replace the simple 180° refocusing pulse with a composite 180° pulse that is broadband with respect to the imperfection that is causing the problem.

Phase-distortionless or constant-rotation composite pulses were introduced for this purpose [5,10,12,15,16]. They have a rotation axis that is approximately constant along (say) the rotating-frame *x* axis across their effective bandwidth. The problem is that this bandwidth is not nearly large enough for the imperfections that are routinely encountered. There are no short phase-distortionless composite 180° pulses that can compensate for a B_1 field that is only a third of its nominal value, or with a resonance offset parameter, $\Delta B/B_1^{nom}$, of 1 or greater. In addition, composite 180° pulses designed to compensate for B_1 inhomogeneity usually have a poor performance with respect to resonance offset, often much worse than that of a simple 180° pulse. So there will always be either parts of the sample or signals with offsets that are outside the usable bandwidth of even the very best phase-distortionless composite pulse. Hence, as we have shown here, if the composite pulse is symmetric or asymmetric, phase distortions will be reintroduced into the spin echo, even if Exorcycle or magnetic field gradients are used to select the echo pathway. We believe that this is the cause of the disappointment that is so often reported when composite refocusing pulses are tried.

Antisymmetric composite pulses have been known for more than 25 years yet very few have yet been proposed [11,12,15], especially for B_1 inhomogeneity. The key favorable property, that the rotation axis always lies in the *xz* plane of the rotating frame, both on and off resonance, has also been recognized for a long time [11]. What we have shown here is that, if one wishes to tackle refocusing pulse imperfections using both coherence pathway selection (as one always should) and composite pulses then an antisymmetric composite pulse must be used. As with any other phase-distortionless composite pulse, the effective bandwidth of this pulse may not be sufficient to cover the full range of the relevant instrumental imperfection but, unlike a symmetric or asymmetric composite pulse, it will not reintroduce phase distortions into the spectrum. We consider that this is a significant result, especially in view of the large number of symmetric and asymmetric sequences that have been proposed.

Acknowledgments

We are grateful to EPSRC for a studentship (S.O.) and to Professor Richard Walton (University of Warwick) for the AlPO-14 sample.

References

[1] M.H. Levitt, R. Freeman, NMR population inversion using a composite pulse, J. Magn. Reson. 33 (1979) 473–476.
[2] R. Freeman, S.P. Kempsell, M.H. Levitt, Radiofrequency pulse sequences which compensate their own imperfections, J. Magn. Reson. 38 (1980) 453–479.
[3] M.H. Levitt, Symmetrical composite pulse sequences for NMR population inversion. II. Compensation of radiofrequency field inhomogeneity, J. Magn. Reson. 48 (1982) 234–264.
[4] M.H. Levitt, Symmetrical composite pulse sequences for NMR population inversion. I. Compensation of resonance offset, J. Magn. Reson. 50 (1982) 95–110.
[5] R. Tycko, Broadband population inversion, Phys. Rev. Lett. 51 (1983) 775–777.
[6] M.H. Levitt, R.R. Ernst, Composite pulses constructed by a recursive expansion procedure, J. Magn. Reson. 55 (1983) 247–254.
[7] A.J. Shaka, R. Freeman, Composite pulses with dual compensation, J. Magn. Reson. 55 (1983) 487–493.
[8] A.J. Shaka, R. Freeman, Spatially selective radiofrequency pulses, J. Magn. Reson. 59 (1984) 169–176.
[9] R. Tycko, A. Pines, Iterative schemes for broadband and narrowband population inversion in NMR, Chem. Phys. Lett. 111 (1984) 462–467.
[10] R. Tycko, H.M. Cho, E. Schneider, A. Pines, Composite pulses without phase distortion, J. Magn. Reson. 61 (1985) 90–101.
[11] R. Tycko, A. Pines, J. Guckenheimer, Fixed point theory of iterative excitation schemes in NMR, J. Chem. Phys. 83 (1985) 2775–2802.
[12] A.J. Shaka, A. Pines, Symmetric phase-alternating composite pulses, J. Magn. Reson. 71 (1987) 495–503.
[13] M.H. Levitt, Composite pulses, Prog. NMR Spectrosc. 18 (1986) 61–122.
[14] R. Tycko, Iterative methods in the design of pulse sequences for NMR excitation, Adv. Magn. Reson. 15 (1990) 1–49.
[15] S. Wimperis, Iterative schemes for phase-distortionless composite 180° pulses, J. Magn. Reson. 93 (1991) 199–206.
[16] S. Wimperis, Broadband, narrowband and passband composite pulses for use in advanced NMR experiments, J. Magn. Reson. A 109 (1994) 221–231.
[17] M.H. Levitt, Composite pulses, in: D.M. Grant, R.K. Harris (Eds.), Encyclopedia of Nuclear Magnetic Resonance, Wiley, Chichester, 1996, pp. 2694–2711.
[18] J.A. Jones, Quantum computing with NMR, Prog. NMR Spectrosc. 59 (2011) 91–120.
[19] M.H. Levitt, R. Freeman, T. Frenkiel, Broadband heteronuclear decoupling, J. Magn. Reson. 47 (1982) 328–330.
[20] J.S. Waugh, Systematic procedure for constructing broadband decoupling sequences, J. Magn. Reson. 49 (1982) 517–521.
[21] A.J. Shaka, J. Keeler, T. Frenkiel, R. Freeman, An improved sequence for broadband decoupling: WALTZ-16, J. Magn. Reson. 52 (1983) 335–338.
[22] T.-L. Hwang, A.J. Shaka, Water suppression that works. Excitation sculpting using arbitrary waveforms and pulse field gradients, J. Magn. Reson. A 112 (1995) 275–279.
[23] O.W. Sørensen, G.W. Eich, M.H. Levitt, G. Bodenhausen, R.R. Ernst, Product operator formalism for the description of NMR pulse experiments, Prog. NMR Spectrosc. 16 (1983) 163–192.
[24] G. Bodenhausen, H. Kogler, R.R. Ernst, Selection of coherence-transfer pathways in NMR pulse experiments, J. Magn. Reson. 58 (1984) 370–388.
[25] G. Bodenhausen, R. Freeman, D.L. Turner, Suppression of artefacts in two-dimensional J spectroscopy, J. Magn. Reson. 27 (1977) 511–514.
[26] M.R. Bendall, R.E. Gordon, Depth and refocusing pulses designed for multipulse NMR with surface coils, J. Magn. Reson. 53 (1983) 365–385.
[27] C. Counsell, M.H. Levitt, R.R. Ernst, Analytical theory of composite pulses, J. Magn. Reson. 63 (1985) 133–141.
[28] M.H. Levitt, R. Freeman, Compensation for pulse imperfections in NMR spin-echo experiments, J. Magn. Reson. 43 (1981) 65–80.